PB83-189704

Analysis of a Wastewater for Seven Priority Pollutant Elements by D.C. Argon Plasma Emission Spectroscopy

(U.S.) Environmental Monitoring and Support Lab.-Cincinnati, OH

1982

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before comple

1. REPORT NO.	2.	3. PB83-139704
EPA-600/J-82-034	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE Journal Article:	5. REPORT DATE
Analysis of a Wastewater for Seven Priority Pollutant Elements by D.C. Argon Plasma Emission Spectroscopy	1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Randall J. Dellefield Theodore D. Martin	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Inorganic Analyses Section Environmental Monitoring and Support Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Journal Article 6/79 to 11/79
	14. SPONSORING AGENCY CODE EPA 600/6

15. SUPPLEMENTARY NOTES
Atomic Spectroscopy Vol. 3, No. 6 165-170, Nov.-Dec. 1982

16. ABSTRACT

This limited project was conducted to determine the usefulness of the D.C. argon plasma for the analysis of wastewater. Seven priority pollutant elements, arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and thallium (Tl), were selected for use in this project. A discussion on the linearity, instrumental detection limit, and stray light effects for each element is included. The report contains precision and accuracy data on a mixed domestic-industrial effluent spiked at three concentrations. The effect of varying the concentration of the matrix buffer and the need for matrix matching of the standard to sample are also discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to public	Unclassified	7
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

Reprinted from Atomic Spectroscopy, Vol. 3, No. 6

EPA-600/J-82-034
JOURNAL ARTICLE

ANALYSIS OF A WASTEWATER FOR SEVEN PRIORITY POLLUTANT ELEMENTS BY D.C. ARGON PLASMA EMISSION SPECTROSCOPY*

Randall J. Dellefield† and Theodore D. Martin
Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

This limited project was conducted to determine the usefulness of the D. C. argon plasma for the analysis of wastewater. Seven priority pollutant elements, arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and thallium (Tl), were selected for use in this project. A discussion on the linearity, instrumental detection limit, and stray light effects for each element is included. The report contains precision and accuracy data on a mixed domestic-industrial effluent spiked at three concentrations. The effect of varying the concentration of the matrix buffer and the need for matrix matching of the standard to sample are also discussed.

RESUME

Ce projet a été exécuté pour déterminer l'utilité d'un plasma argon D.C. dans l'analyse d'eau résiduaire. Nous avons sélectionné 7 polluants prioritaires, Arsenic (As), Beryllium (Be), cadmium (Cd), chrome (Cr), nickel (Ni), plomb (Pb), et thallium (Tl) pour ce projet. Nous présentons une discussion de la linéarité, de la détection limite et des effets de lumière diffuse pour chaque élément. Le rapport contient des données de précision et d'exactitude sur un effluent mixte domestique/industriel soumis à 3 ajouts différents. Nous commentons également l'effet de variation de la concentration de la matrice et les besoins de concordance des matrices du standard et de l'échantillon.

ZUSAMMENFASSUNG

Dieses begrenzte Projekt wurde durchgeführt, um die Einsetzbarkeit des DC-Argonplasmas für die Abwasseranalytik zu prüfen. Sieben umweltrelevante Elemente wurden für dieses Projekt ausgewählt; Arsen (As), Beryllium (Be), Blei (Pb), Cadmium (Cd), Chrom (Cr), Nickel (Ni) und Thallium (Tl). Für jedes Element werden die Linearität, die instrumentelle Nachweisgrenze und Streulichteffekte diskutiert. Der Bericht enthält Daten über Genauigkeit und Richtigkeit bei einem gemischten häuslichen und industriellen Abwasser, das mit drei Konzentrationen aufgestockt wurde. Der Effekt verschiedener Konzentrationen an Matrixpuffer sowie die Notwendigkeit, die Matrix in den Bezugslösungen den Proben anzugleichen, wird ebenfalls diskutiert.

INTRODUCTION

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory–Cincinnati has as one of its activities the development and evaluation of techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste. The following is a discussion on the usefulness of direct current argon plasma spectroscopy for the determination of a limited number of priority pollutant elements in wastewater. The instrument used for this work was a Spectrametrics SpectraSpan III, which employs a direct current argon plasma emission source and an echelle grating spectrometer to resolve the emitted light into the analytical wavelengths of interest. Although some models of this instrument have the capability of simultaneously analyzing 20 wavelengths, the model utilized in this project was a sequential instrument.

Seven priority pollutant elements, as well as calcium (Ca) and magnesium (Mg), were selected for this work. Some are characteristically easy and others difficult to determine by emission spectroscopy techniques. The elements and the wavelengths used are listed in Table I.

The analytical wavelengths for each element were recommended by Spectrametrics. All of the samples, standards, and blanks run were in a 2% LiCl (3200 mg/L Li), 0.5% (v/v) HNO_3, 0.5% (v/v) HCl matrix.

TABLE I
Elements Determined and Wavelengths

Element	*Wavelength (nm)*
As	193.70
Be	234.86
Ca	396.85
Cd	228.80
Cr	357.87
Mg	279.55
Ni	341.48
Pb	405.78
Tl	351.92

EXPERIMENTAL

Listed below are the specifications and recommended operating parameters for the Spectrametrics SpectraSpan III, a sequential emission spectrometer equipped with SpectraJet III, a three-electrode argon plasma system.

Instrument Parameters and Operating Conditions

1. Aerosol Generator

A ceramic pneumatic nebulizer was used to aspirate the sample. The liquid flow rate of 2.34 mL/min into the nebulizer was controlled by a peristaltic pump. An argon flow rate of approximately 6 L/min was delivered to the nebulizer at 21 psig. Large droplets from the

*This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

†Present address: Weirton Steel Division, National Steel Corporation, Weirton, West Virginia 26062.

nebulizer were removed by impingement on the walls of the "inverted flow" nebulization chamber and drained away. Drainage was accomplished by the peristaltic pump. The average drainage flow rate was 2.15 mL/min. Resulting aerosols were delivered to the plasma through a vertical tapered quartz sample introduction tube with an exit diameter of 5 mm.

2. D. C. Plasma Assembly

   A retrofitted three-electrode SpectraJet III unit was used as the plasma source. The two bottom anodes were in an inverted "V" arrangement with graphite electrodes. The top cathode was perpendicular to the anodes and was kept approximately 2 cm above the intersection of the "V" of the two anodes. The cathode utilized a thoriated tungsten electrode. The image of this configuration on the entrance slit was that of an inverted "Y". All three electrodes were surrounded by ceramic sleeves to contain the argon flow. The argon flowed through the sleeves at 1.2 L/min and was delivered at 50 psig. Electrical power to sustain the plasma was 14 amps at 70 volts D.C. Cooling water for the source was supplied by a submersible pump in a 10-gallon water reservoir.

3. Plasma Observation Height

   The spatial profile of the plasma was peaked horizontally and vertically for each element of interest. The usual area of observation was approximately 1 mm below the intersection of the three plasma legs.

4. Spectrometer

   The SpectraSpan III is a direct reading sequential 0.75-m modified Czerny-Turner mount spectrometer. An echelle grating having 79 grooves/mm and a prism for order separation are combined to give a high-resolution optical system.

   a. Slit Openings. Entrance: 300 μm vertical; 50 μm horizontal. Exit: 300 μm vertical; 75 μm horizontal. (Recommended by Spectrametrics for routine use.)

   b. Photomultiplier. Hamamatsu R-292

5. Data Acquisition System

   The system and signal amplifier are microprocessor-controlled, with a two-point calibration set through the front panel. Ten-second integrations were used with three integrations per sample and standard.

6. Data Output

   A Texas Instruments Silent Writer, Model 700, was used for hard-copy output.

Standards and Reagents

All stock standard solutions were prepared from analytical reagent grade chemicals at a 1000-mg/L concentration. The HNO_3 and HCl used were redistilled for purity. Other chemicals used were also of reagent grade quality. The water used to dissolve and dilute reagents was equivalent to ASTM Type II reagent grade water.

General Operating Procedures

In order to achieve reproducible results on a daily basis, it was necessary to change certain instrument parts regularly. The two graphite anodes, the tungsten cathode, and three ceramic sleeves were usually changed daily. To ensure smooth pumping, the Tygon peristaltic pump tubing was changed semiweekly. The nebulizer itself was replaced after showing erratic data from the aspiration of the standard and had to be replaced approximately every 45 operating hours. Replacement was necessary because it was impossible to clean the nebulizer adequately to restore its original performance. The nebulizer problem occurred following the aspiration of high Ca or Mg concentrations (>300 mg/L) and resulted in a gradual decrease in intensity response requiring that the gain on the photomultiplier tube be increased. The occurrence was predictable and verified by analyzing a check standard whose intensity was known from a prior analysis. Once nebulizer performance was affected, restandardization was required. The continued analysis of samples causing this problem would necessitate more frequent instrument calibration.

In order to become thermally stable the instrument was allowed to operate for at least one hour before standardization. The wavelength of interest was then peaked optically by moving both the grating and prism. This was accomplished while aspirating a high standard of approximately 100 mg/L and maximizing the signal on an analog meter. Then, in a similar fashion, the plasma would be adjusted horizontally and vertically to maximize the signal.

Before calibration the instrument was autoranged while nebulizing the standard solution. The microprocessor selected one of two capacitors and a gain setting to give a signal of approximately 8000 mV. For calibration, the standard and blank were then nebulized and their intensities measured utilizing the same gain setting. These two values were stored in the memory and used for the calculation of sample concentrations by linear interpolation. During the analysis of samples, the calibration standard was nebulized approximately every three samples to check for instrument drift. The instrument was restandardized whenever the resulting concentration exceeded ±3% of the standard concentration.

RESULTS AND DISCUSSION

To analyze the wastewater properly, the detection limit and linear working ranges for each of the listed wavelengths needed to be verified. It was necessary to determine the linearity of each analytical wavelength since any self-absorption that occurred in the plasma would result in a nonlinear calibration curve. Any bending of the calibration curve cannot be managed by an instrument which uses a two-point calibration curve.

Linearity

The linearity of each element was determined by standardizing at 100 mg/L and then analyzing successively lower standards. These standards were 50, 10, 5, 1, 0.5, 0.1, 0.05, 0.01, 0.005 . . . mg/L. The lower limit for the analysis of standards was the Spectrametrics detection limits. Each standard concentration was plotted versus its mV intensity, minus the blank mV intensity. Of the seven elements investigated only the cadmium line was not linear to 50 mg/L with apparent curvature in calibration above 5 mg/L. For this reason, cadmium (228.80 nm) could not be determined above 5 mg/L.

Detection Limit

The instrumental detection limits for a 2% LiCl matrix were determined using two different methods. The first was based on the standard deviation measurement about the blank. The instrument was first calibrated at 10 mg/L. This was done for all elements except As and Cd. (It was necessary to calibrate As at 100 mg/L because of low sensitivity and critical plasma alignment; Cd was calibrated at 5 mg/L, the limit of linearity). Subsequent to each calibration the blank matrix solution was analyzed ten times using 10-sec integrations. The detection limit was calculated to be three times the standard deviation of the reagent blank measurements ($3SD_{RB}$).

The second approach used was the Method Detection Limit (MDL) (1) and is defined as follows for the 99% confidence level:

$$MDL = 3.14 \left[(SD_{LCS})^2 - (SD_{RB})^2 \right]^{0.5}$$

where:

SD_{RB} is the standard deviation of the reagent blank

SD_{LCS} is the standard deviation of seven replicate aspirations of the laboratory control standard (LCS). The concentration of the LCS was three to five times the Spectrametric detection limits.

The detection limits for each method and also those as published by Spectrametrics are given in Table II. The detection limits calculated by both methods are similar and agree relatively well with those published by Spectrametrics, with As being the only exception.

TABLE II
Instrumental Detection Limits (μg/L) for a 2% LiCl Matrix

Element	*Wavelength (nm)*	*MDL*	*3 SD_{RB}*	*SMI[a]*
As	193.70	1300	2000	500
Be	234.86	1.0	1.2	1.0
Cd	228.80	12	12	5
Cr	257.87	3	3	2
Ni	341.48	6	6	10
Pb	405.78	20	12	50
Tl	351.92	22	24	

[a]Data from Spectrametrics Incorporated.

Precision and Accuracy

Precision and accuracy data were gathered by analyzing a mixed domestic-industrial secondary effluent from a wastewater treatment plant. Four concentration levels of analyte were prepared in the sample matrix, each having seven digested replicate samples. Each replicate sample was prepared using 100 mL of effluent subjected to a vigorous nitric acid digestion (2). The first level was the unspiked effluent, and the other three levels were spiked before digestion with increasing amounts of the analytes measured. Spiking levels are given in Table III. These samples were then analyzed using the wavelengths listed in Table I and the previously stored standards data. Each sample was nebulized once using three 10-sec integrations with the average value used for the determination.

Primarily because of work done by Johnson, Taylor, and Skogerboe (3), the stray light effects of Ca and Mg on each channel were determined before calculating the precision and accuracy of the analyses. The additive spectral interference effect from As on the 228.8-nm line of Cd also had to be determined before the final precision and accuracy calculations were made.

TABLE III
Spike Levels of Digested Effluent Samples

Element	*Spike 1 (mg/L)*	*Spike 2 (mg/L)*	*Spike 3 (mg/L)*
As	1.94	9.67	96.75
Be	0.20	1.00	10.00
Cd	0.10	0.50	5.00
Cr	0.20	1.00	10.00
Ni	0.20	1.00	10.00
Pb	0.24	1.20	12.00
Tl	0.20	0.98	9.80

Stray Light Effects

The stray light effects for both Ca and Mg were determined by analyzing 50-, 100-, 300-, and 500-mg/L single-metal solutions of Ca and Mg. Each solution was prepared using deionized distilled water in the 2% (w/v) LiCl, 0.5% (v/v) HCl, 0.5% (v/v) HNO_3 matrix. After standardizing each analyte with a 1.0-mg/L concentration of the element, the Mg and Ca solutions were analyzed. The resulting concentrations for Cr, Ni, Pb, and Tl were plotted as stray light equivalents versus Ca or Mg concentration. It should be noted that both the Ca and Mg solutions were analyzed by inductively coupled and D. C. plasma spectroscopy for all seven analytes and were found to be below the detection limits. The stray light equivalents for these element wavelengths were determined to be linear. This agreed with the work done by Johnson et al. for Be, Ni, and Pb; however, the other four elements were not examined by them. Table IV gives the stray light equivalents for 500 mg/L of Ca and Mg. Thus, any Ca and/or Mg in a sample, especially if concentrated by evaporation, would definitely have an effect on the calculated concentration of some analytes and must be taken into consideration. This was evident in the digested secondary effluents spikes. Unfortunately, Ca (396.85 nm) was only linear up to 15 mg/L; therefore, these samples had to be diluted to determine the Ca concentration. Dilution would be necessary for any sample with a Ca concentration greater than 15 mg/L unless another wavelength was used.

The digested wastewater samples were then analyzed to determine the amount of stray light being produced by Ca and Mg. The average Ca and Mg concentration in these samples was 82 and 21 mg/L, respectively. The stray light equivalent was then calculated and subtracted from the value found for the spiked and nonspiked samples.

It can be seen from Table IV that for some of these metals, neither Ca nor Mg caused any interference. However,

CONCLUSION

The precision and accuracy results for some elements from the wastewater analysis and the detection limits achieved give some indication of the applicability of this technique to wastewater analysis. The results of this investigation also point out the necessity for either matrix matching the standard to that of the sample or ensuring that adequate correction is made for any matrix interference effects. Although the stray light effect can be removed by background correction in newer instruments, matching the standard to the sample matrix is still required.

ACKNOWLEDGMENT

The authors of this report are grateful to Mr. John F. Kopp and Gerald D. McKee for their review and advice in the preparation of this report.

Received June 7, 1982

REFERENCES

1. J. Glaser, D. Foerst, G. McKee, S. Quave, and W. Budde, Environ. Sci. Technol. **15**, 1426 (1981).
2. "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Atomic Absorption Methods, Section 4.1.3, U.S. EPA, Environmental and Monitoring Support Laboratory – Cincinnati (1979).
3. G. W. Johnson, H. E. Taylor, and R. K. Skogerboe, Spectrochim. Acta **34B**, 197 (1979).
4. G. W. Johnson, H. E. Taylor, and R. K. Skogerboe, Appl. Spectrosc. **34**, 19 (1980).

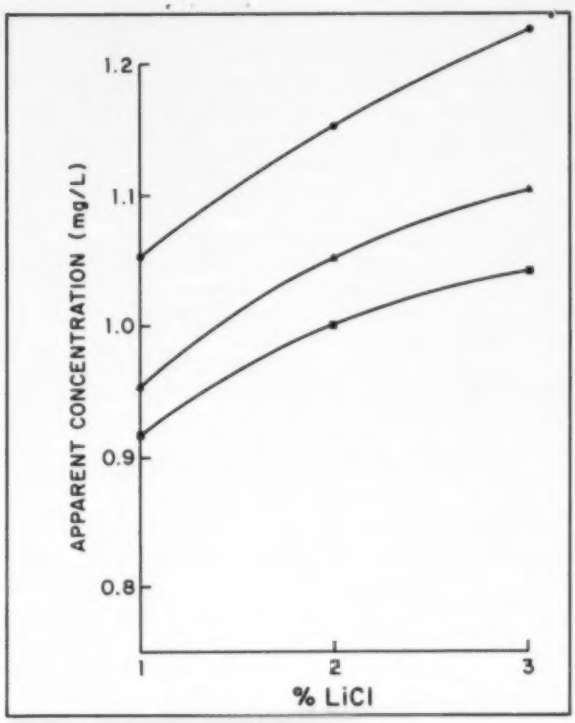


Fig. 5. 1 mg/L Pb in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution

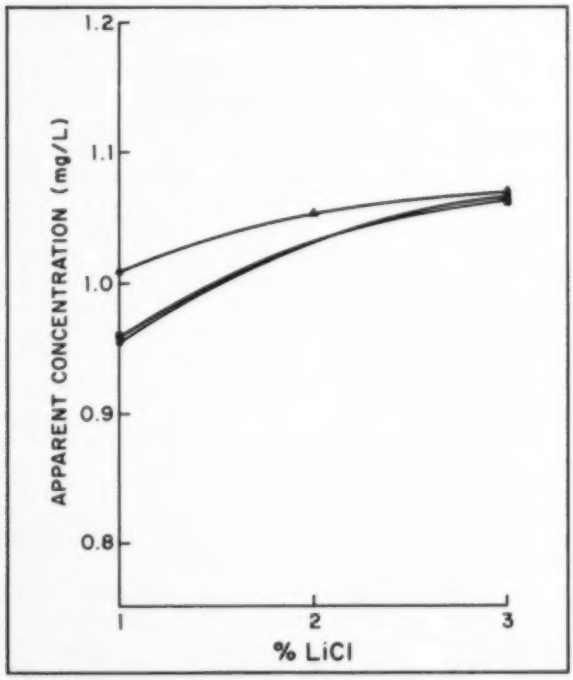


Fig. 4. 1 mg/L Cr in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution

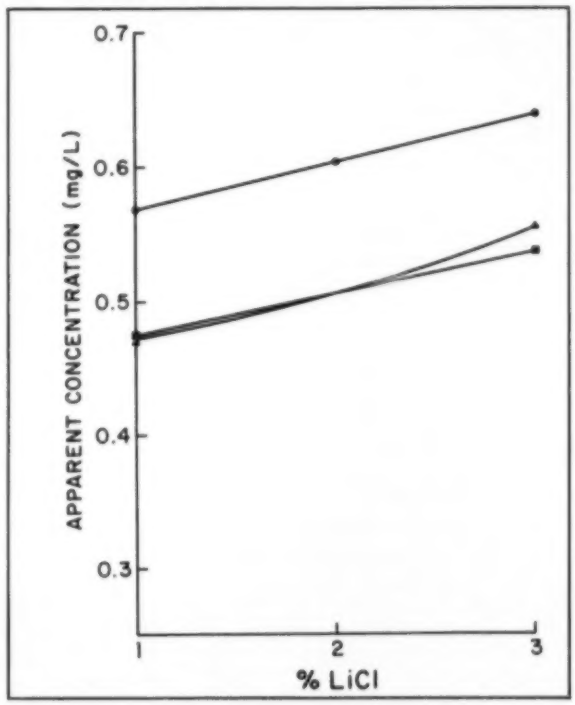


Fig. 6. 0.5 mg/L Tl in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution

TABLE IV
Stray Light Equivalents (SLE) for 500 mg/L of Ca and Mg

Element	*Wavelength (nm)*	*SLE-Ca (µg/L)*	*SLE-Mg (µg/L)*
As	193.70	0	0
Be	234.86	0	0
Cd	228.80	0	0
Cr	357.87	4	0
Ni	341.48	15	3
Pb	405.78	214	30
Tl	351.92	86	12

for Pb in these samples, there was a definite interference.

The amount of additive interference on the 228.80-nm line of Cd that could be attributed to a high As concentration was determined by analyzing a 100-mg/L As standard on the standardized Cd line. This concentration resulted in a spectral interference effect (SIE) equivalent to 417 µg/L Cd. Because this was a linear interference, it was concluded that this Cd equivalent for 100 mg/L As would be the upper limit for a subsequent calculation of an As SIE for Cd. Therefore, knowing the amount of As in each sample and spike, the SIE value was calculated and subtracted from the Cd concentration.

Table V shows the precision and accuracy for the digested secondary effluent and its three spike levels. The means reported are for seven digested replicates at each level minus any stray light or spectral interference effect.

The precision can be considered very good at the upper levels, but deteriorates for some of the nonspiked samples, primarily because those levels were so close to the detection limit. The instrument was calibrated at 10 mg/L which was near the upper spiking range except for As and Cd which were calibrated at 100 mg/L and 5 mg/L, respectively. The precision for the lower range samples should improve slightly if the calibration were performed at a concentration of 0.5 mg/L. This would reduce the effect of any fluctuation in the plasma emission which when multiplied by the concentration factor could cause large deviations in sample concentration. Although for some elements, decreasing the standard concentration would increase the frequency of restandardization required.

The accuracy reflected in the percent recovery is good; however, the data would indicate that accuracy would be improved if the instrument were calibrated near the expected sample concentration.

Sample Concentration Dependence on LiCl Concentration

Characteristic of a D. C. excitation source is the fact that it must be buffered. One of the most common buffering elements is lithium. The purpose of the Li was to stabilize the plasma and to provide an excess electron population to reduce any multiply charged ions (3, 4). In this work, the Li was added as LiCl. Since buffering a solution with LiCl adds another variable, two concerns were investigated:

1. the effect of varying concentrations of LiCl on the intensity of an analyte
2. the effect of large concentrations of an easily ionized alkaline earth metal (Ca and Mg) on the excitation of an analyte

To determine these effects, three sets of three solutions each were prepared to contain 990 µg/L Be, 1000 µg/L Cd, Cr, Ni, and Pb, and 490 µg/L Tl. In one set, the Ca concentration was made 500 mg/L, and in a second the Mg concentration was made 500 mg/L. The third set was used as a control. All three were buffered with varying concentrations of LiCl. One solution in each set was buffered with 1600 mg/L Li or 1% LiCl, another with 3200 mg/L Li or 2% LiCl, and the third with 4800 mg/L Li or 3% LiCl. All solutions were diluted to final volume using deionized distilled water containing 0.5% (v/v) HNO_3 and analyzed using single-metal standards, with both the standards and blank solutions buffered at 2% LiCl. After the results for Pb, Ni, and Tl had been corrected for Ca and Mg stray light interferences, they were plotted versus LiCl concentration.

The results of this phase of the investigation revealed that as the LiCl concentration changed, the emitted intensity of the analytes examined also changed. The intensity

TABLE V
Precision and Accuracy for Digested Secondary Effluents

Element and spike	*Mean (mg/L)*	*Standard deviation*	*%RSD*	*% Recovery of spike*
As-Sample	0.282	0.147	52	
As-Spike 1	1.82	0.140	8	79
As-Spike 2	10.0	0.241	2	101
As-Spike 3	99.0	2.50	3	102
Be-Sample	0.0			
Be-Spike 1	0.197	0.004	2	99
Be-Spike 2	1.06	0.024	2	106
Be-Spike 3	10.1	0.151	1	101
Cd-Sample	0.021	0.007	31	
Cd-Spike 1	0.096	0.008	7	75
Cd-Spike 2	0.54	0.014	2	104
Cd-Spike 3	4.92	0.098	1	98
Cr-Sample	0.084	0.014	17	
Cr-Spike 1	0.273	0.006	2	95
Cr-Spike 2	1.13	0.028	2	105
Cr-Spike 3	10.2	0.116	1	101
Ni-Sample	0.145	0.012	8	
Ni-Spike 1	0.336	0.008	2	96
Ni-Spike 2	1.14	0.015	1	100
Ni-Spike 3	10.0	0.121	1	99
Pb-Sample	0.132	0.007	4	
Pb-Spike 1	0.352	0.008	2	92
Pb-Spike 2	1.29	0.025	2	97
Pb-Spike 3	12.3	0.126	1	101
Tl-Sample	0.039	0.028	50	
Tl-Spike 1	0.210	0.008	4	87
Tl-Spike 2	0.98	0.026	3	96
Tl-Spike 3	10.0	0.250	3	102

of the analyte was directly proportional to the LiCl concentration. It should be noted, however, that since deionized distilled water gave the same background level as a 2% (w/v) LiCl blank, this increase in intensity was not due to an increase in the background level (Figures 1–6). It was concluded that the LiCl concentration should be at least 2% (w/v) but not more than 3% (w/v). The addition of more than 3% (w/v) LiCl did not substantially increase the intensity, as determined from the curves beginning to "bend off."[1] With less than 2% (w/v) LiCl the amount of ionization buffering was not sufficient for a matrix containing high dissolved solids. Thus, a primary concern would be to maintain approximately the same Li concentration in both standards and samples (±10%). It should be noted that the LiCl was analyzed by two spectroscopic techniques, and it was verified that the LiCl was free of any significant analyte concentrations that could cause an increase in intensity.

It was further observed that the addition of 500 mg/L of Ca or Mg resulted in either a suppression or enhancement of the analyte. Calcium suppressed Be, Cd, and Pb and enhanced Ni and Tl, while Mg enhanced Cd, Cr, Ni, and Pb. This effect is thought to be due to a change in the plasma profile or temperature of the plasma and not that of a stray light effect. The effect of 500 mg/L of Ca on Be confirms this. The Be was suppressed approximately 80 μg/L regardless of the LiCl concentration. Lead experienced a suppression as can be shown by the difference between its stray light equivalent of 214 μg/L Pb for 500 mg/L Ca and the increase of only 150 μg/L Pb in the set of solutions containing 500 mg/L Ca over that set which had no Ca or Mg. If there were no suppression of the Pb by Ca in the plasma, then the increase in intensity should have been 214 μg/L not 150 μg/L. Calcium had the greatest matrix effects, and greater concentrations of LiCl did not significantly reduce any suppression.

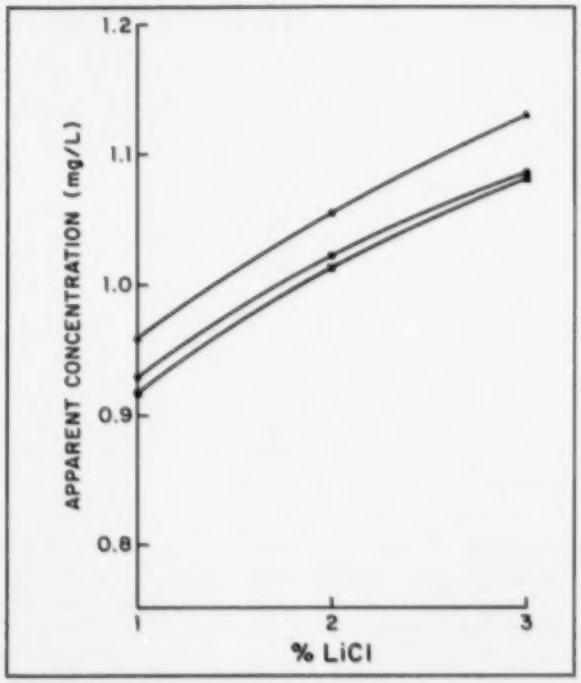


Fig. 1. 1 mg/L Cd in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution

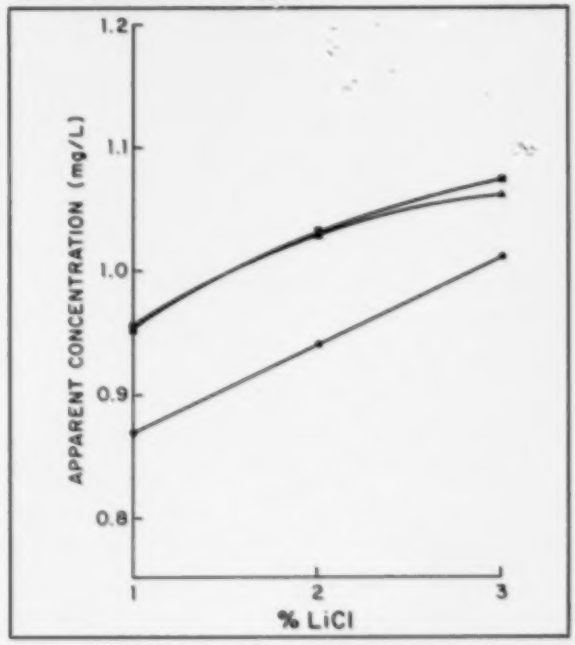
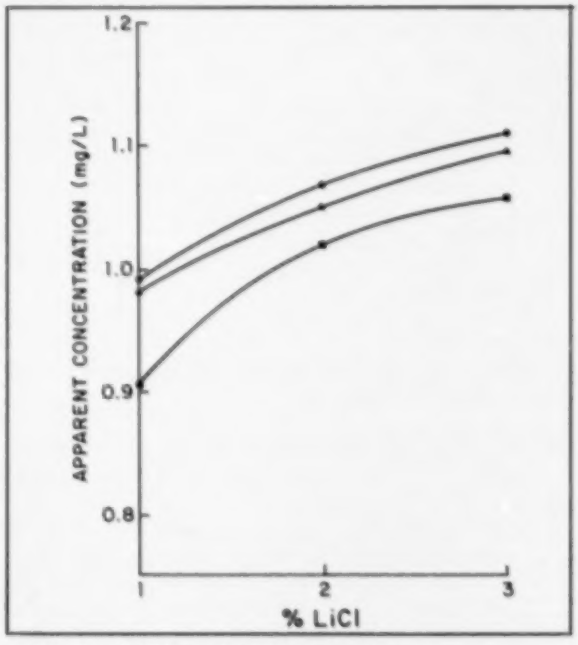


Fig. 2. 1 mg/L Be in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution



g. 3. 1 mg/L Ni in varying LiCl concentrations.
▲ Data points for 500 mg/L Mg + spike solution
● Data points for 500 mg/L Ca + spike solution
■ Data points for spike solution